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(54) DENTIFRICES

(71) COLGATE-PALMOLIVE COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of 300 Park Avenue, New York, New York 10022, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to dentifrices.

According to this invention a dentifrice contains non-toxic iridescent or pearlescent flakes.

Transparent toothpastes generally contain a dental vehicle which forms a gel or creamy mass of a consistency which can be extruded from a collapsible tube such as an aluminium tube or a lead tube. The vehicle, often referred to as a gelled vehicle, usually contains liquids and solids. In general, the liquid comprises water and/or a humectant such as glcerine, sorbitol, propylene glycol or polyethylene glycol 400 or a suitable mixture thereof. It is usually advantageous to use a mixture of water and one or two humectants. The total liquid content is generally in the range 20% to 90% by weight of the vehicle. The preferred humectants are glycerine and sorbitol. Typically the vehicle contains 0 to 80% by weight of glycerine, 20 to 80% by weight of sorbitol and 20 to 80% by weight of water.

The solid portion of the vehicle is a gelling agent, such as a natural or synthetic gum or gum-like material, such as Irish Moss, gum tragacanth, an alkali metal (e.g. lithium, potassium or sodium) carboxymethyl cellulose or hydroxymethyl carboxyethyl cellulose, polyvinyl pyrrolidone, starch, a water-soluble hydrophilic colloidal carboxyvinyl polymer such as those sold under the trademark "Carbopol" 934 and 940, hydroxyethyl cellulose, Indian gum, acacia gum, agar agar, locust bean gum, "Laponite" CP or SP which are synthetic inorganic complex silicate clays sold under trademark by Laporte Industries, Ltd., or pectin or inorganic thickeners such as colloidal silicas, e.g. synthetic finely divided silicas including those sold under the trademarks "Cab-O-Sil M5", "Syloid 244", "Syloid 266" and Aerosil D200". The solid portion of the vehicle is typically present in an amount up to 10% by weight of the toothpaste and preferably 0.5% to 5% by weight.

The art is well aquainted with the formulation of transparent dental gelled vehicles and the adjustments in composition needed to promote transparency. For instance, it is known that the presence of flavouring materials insoluble in the system will decrease transparency and that appropriate changes, e.g. in the surface active agent system, to increase the solubility of such flavouring materials will increase transparency.

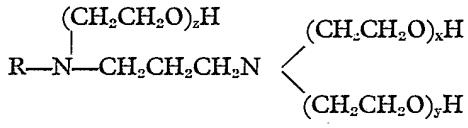
The transparent toothpaste preferably also contains a dental polishing agent. The type and proportion of this polishing agent should be such as not to destroy the transparency of the toothpaste. One particularly suitable material is a porous amorphous silicic anhydride having an average particle size in the range 1 to 65 microns, a surface area of 200 to 450 m^2/g and a bulk density of 0.15 to 0.30 g/cm^3. Such an amorphous silicic anhydride contains but little water, typically about 5% or less, and is often referred to as a dehydrated silica gel. The preferred grades of amorphous silicic anhydride polishing agent are "Syloid 72" and "Syloid 74" which are described in "The Davison Family of Syloid Silicas" published by their manufacturer, Grace, Davison Chemical Co., U.S.A., "Santocel 100", manufactured by Monsanto, is also a desirable polishing agent. "Syloid 72" has an average particle size of about 4 microns, a surface area of about 340 m^2/g and a bulk density of about 0.177 g/cm^3. "Syloid 74" has an average particle size of about 8 microns, a surface area of about 321 m^2/g and a bulk density of about 0.6 g/cm^3. A grade of "Santocel 100" has an average particle size of 46 to 64 microns, a surface

area of about 239 m^2/g and a bulk density of about 0.24 g/cm^3. These amorphous silicic anhydrides may be used singly or as mixtures. They are typically employed in an amount in the range 5% to 50%, preferably 10% to 20% by weight of the tranparent toothpaste. The maximum particle size in the preferred grades of amorphous silicic anhydride polishing agent is desirably below the minimum size of palpability and is typically less than 75 microns. It is within the scope of the invention to use other polishing agents, particularly those which have a refractive index similar to that of the vehicle.

An additional highly desirable polishing agent which may be added to the gel vehicle is a complex sodium alumino-silicate which has a refractive index of 1.44 to 1.47, a mol ratio of silica to alumina of about 7:1, up to 20% by weight of moisture and up to 10% by weight of sodium oxide. Typically, this material has a particle size of up to 35 microns, preferably 1 to 20 microns. The preferred moisture content is 10% to 20% by weight, measured by loss at 105°C, and the typical content of sodium oxide is 5% to 10% by weight. Generally, the agent has a loose bulk density of up to 0.2 g/cc, preferably 0.07 to 0.12 g/cc.

The transparent toothpaste may also contain a surface active agent system, e.g. to achieve increased propylactitc action and to assist in achieving thorough and complete dispersion of the composition throughout the oral cavity. The surface active agent may be anionic, nonionic, ampholytic or cationic in nature, and it is preferred to employ as the surface active agent a detersive material which imparts to the composition detersive and foaming properties. Suitable types of such detergents are water-soluble fatty acid monoglyceride of monosulphates, such as sodium monosulphated monoglyceride of hydrogenated cocount oil fatty acids, alkyl sulphates such as sodium lauryl sulphate, alkyl aryl sulphonates such as sodium dodecyl benzene sulphonate, alkyl sulphoacetaes, fatty acid esters of 1,2 hydroxy propane sulphonates and substantially saturated aliphatic acyl amides of aliphatic amino carboxylic acid compounds, such as those having 12 to 16 carbons in the fatty acid, alkyl or acyl radicals. Examples of the last mentioned amides are N-lauroyl, sarcosine and the sodium, potassium and ethanolamine salts of N-lauroyl, M-myristoyl or N-palmitoylsarcosine, which should be substantially free from soap or similar higher fatty acid material which tends to reduce substantially the effect of these compounds. The use of these sarcosine compounds in the dentifrice compositions of the present invention is particularly advantageous since these materials exhibit a prolonged and marked effect in the inhibition of acid formation in the oral cavity due to carbohydrate breakdown, in addition to exerting some reduction in the solubility of tooth enamel in acid solutions.

Other particularly suitable surface active agents are nonionic agents such as condensates of sorbitan monostearate with approximately 60 moles of ethylene oxide, condensates of ethylene oxide with propylene oxide, condensates of propylene glycol and amphoteric agents such as quaternized imidazole derivatives which are available under the trademark "Miranol" such as "Miranol C_2M". Cationic surface active germicides and antibacterial compounds such as di - isobutylphenoxyethoxyethyl dimethyl benzyl ammonium chloride, benzyl dimethyl stearyl ammonium chloride, tertiary amines, having one fatty alkyl group (of from 12 to 18 carbon atoms) and two (poly) oxyethylene groups attached to the nitrogen (typically containing a total of from 2 to 50 ethanoxy groups per molecule) and salts thereof with acids, and compounds of the structure



where R is a fatty alkyl group containing from 12 to 18 carbon atoms, and x, y and z total 3 or higher, as well as salts thereof with mineral organic acids, may also be used.

It is preferred that the total amount of surface active agent be in the range 0.5% to 5% by weight, preferably 1% to 3%, of the dentrifice.

Various other materials may be incorporated in the dentrifice. Examples are colouring or whitening agents, preservatives, silicones, chlorophyll compounds, and ammoniated materials such as urea, diammoniumphosphate and mixtures thereof. Each of these adjuvants may be typically incorporated in the dentrifices in amounts up to 5% by weight.

The dentifrice may also contain antibacterial agents, usually in amounts of 0.01% to 5% by weight. Typical examples of such

agents are guanidines, biguadines and amines such as:

N^1 - (4 - chlorobenzyl) - N^5 - 2,4 - (dichlorobenzyl) biguanide;
p - chlorophenyl biguanide;
4 - chlorobenzhydryl biguanide
4 - chlorobenzhydrylguanylurea;
N - 3 - lauroxypropyl - N^5 - *p* - chlorobenzylbiguanide;
1,6 - di - p - chlorophenylbiguanidohexane;
1 - (lauryldimethylammonium) - 8 - (*p* - chlorobenzyldimethyl ammonium) octane dichloride;
5,6 - dichloro - 2 - guanidinobenzimidazole;
N^1 - *p* - chlorophenyl - N^5 - laurylbiguanide;
5 - amino - 1,3 - bis (2 - ethylhexyl) - 5 - methylhexahydropyrimidine;

and their non-toxic acid addition salts.

Suitable flavouring or sweetening sialagogues may be employed. Examples of suitable flavouring agents are flavouring oils, e.g. oils of spearmint, peppermint, wintergreen, sassafras, clove, sage, eucalyptus, majoram, cinnamon, lemon and orange, as well as sodium methylsalicylate. Suitable sweetening agents include sucrose, lactose, maltose, sorbitol and saccharin. Suitably, flavour and sweetening agent may together constitute from 0.01% to 5% by weight or more of the dentifrice. Chloroform may be employed to modify the flavour.

The dentifrices may also contain a fluorine-containing compound having a beneficial effect on the care and hygiene of the oral cavity, e.g. diminution of enamel solubility in acid and protection of the teeth against decay. Examples are sodium fluoride, stannous fluoride, potassium stannous fluoride ($SnF_2.KF$), sodium hexafluorostannate, stannous chlorofluoride, sodium fluorozirconate and sodium monofluorophosphate. These materials, which dissociate or release fluorine containing ions in water, suitably may be present in an effective but non-toxic amount, usually within the range 0.01% to 1% by weight calculated on the water-soluble fluorine content thereof.

The iridescent flakes are generally present in amount of from 0.1% to 5%, preferably less than 3%, of the weight of the transparent toothpaste in which they are dispersed. A particularly suitable product is obtained when the iridescent flakes are mother of pearl flakes (a true nacreous secretion found on the inner surfaces of oyster shells and made up of nontoxic calcium carbonate). These mother of pearl flakes refract light in various wave lengths across the colour spectrum and their incorporation in the transparent toothpaste (e.g. in proportions in the range of 1.5% to 3%, preferable about 2%, for example 1.75% to 2.25%) results in a multicoloured speckled effect with the clarity of transparent gel intact, giving a beautiful sparkle. In use, when one extrudes the product from a conventional toothpaste tube onto a toothbrush, the resulting extrudate (which usually has a thickness in the range 4mm to 8mm) is typically clear with visible spaced light-refracting sparkling dots; as the extrudate is moved relative to the eye of the observer, different dots become visible and the apparent colours of individual dots change. Preferable the non-toxic iridescent or pearlescent flakes, e.g. mother of pearl flakes, are of less than 590 micron particle size. Especially good results have been obtained with mother of pearl flakes screened so that they are retained on a 100 mesh (U.S. Standard) sieve (corresponding to a particle size of about 149 microns) and pass through a 30 mesh sieve (corresponding to a particle size of about 590 microns) with the predominant portion being larger than 200 microns.

The mother of pearl flakes can be produced by grinding oyster shells and separating the mother of pearl flakes from the balance of the ground material, e.g. by flotation. Typically, the mother of pearl flakes are flat, smooth-surfaced, less than 50 microns thick (e.g. 10 to 40 microns), oval-shaped in plan view, and made up of numerous thin parallel layers (e.g. of thickness well below a micron to, say, 2 to 3 microns).

Another type of iridescent flake comprises thin transparent mica flakes coated with a thin layer of titanium dioxide (TiO_2). One type of such flakes has a TiO_2 content of about 17%, an average thickness of less than 1 micron (e.g. 0.7 micron), with the longest dimension of most of the flakes being less than 100 microns, e.g. 15 to 40 microns, the refractive index of the TiO_2 layer being about 2.3. When these are incorporated into the transparent toothpaste in a proportion in the range from 0.1% to 0.3% by weight, preferably about 0.25% by weight, the extrudate from the toothpaste tube is also sparkling, with the individual reflecting and iridescent dots being very small and close together, giving an overall opaque pearlescent effect.

Still another, but less desirable, type of iridescent flake comprises mica flakes carrying a coating of another material (e.g. BiOCl) whose refractive index is different from that of the mica.

By variation in particle concentration one can produce different effects. One may also use mixtures of various types of the flakes.

It is found, surprisingly, that the presence of the iridescent flakes not only imparts an unusual appearance but also gives a substantial improvement in the properties of the

dentifrice, such as its ability to remove stains from the teeth.

The transparent toothpaste may be prepared in well known manner. Thus, a gelling agent such as sodium carboxymethyl cellulose or "Carbopol 934" and a preservative such as sodium benzoate, if employed, is dispersed with a humectant such as glycerine. Water may also be present. Additional humectant and water, as an aqueous 70% sorbitol solution, may then be mixed with the dispersion and heat applied at 40 to 65°C, say 50°C, to form a paste, gel or cream. Polishing agent is then added. Surface active agent, such as sodium lauryl sulphate, if employed, is then dispersed in the mixture. The preparation is then cooled and flavour may be added.

The iridescent flakes are then dispersed in the toothpaste with minimal mechanical agitation, insufficient to break them down substantially. The dentifrice is then thoroughly deaerated (e.g. in vacuo) and filled into tubes.

In the manufacture of dentifrices, it is conventional to remove entrained air from the product by de-aeration under vacuum, typically at a late stage in the manufacture. It has been observed that in clear dentifrice gels of suitable viscosity, the dispersed, immobile air bubbles enhance the appearance of the dentifrice, and can, therefore, be permitted to remain. Alternatively, the air can be replaced with another gas in non-toxic quantity, such as nitrogen or carbon dioxide. In particular, carbon dioxide can provide an effervescent character to the dentifrice.

If it is desired to have a minimum amount of air in the detifrice, or only to have to remove a minimum amount of air from the dentifrice, the "Unimix" apparatus described in "Process Engineering" September 11, 1970, pages 81—85, is particularly efficacious for this purpose. In this apparatus a mixing tool can be rotated in clockwise or counterclockwise manner, and the action of the mixing tool is followed by the action of a scraper blade to ensure that the working surface of the apparatus is scraped clean. Preferably, a plastics material such as polytetrafluoroethane is used as the scraper since it is compatible with the various ingredients of the dentifrice. The positioning of the mixing tool and the scraper from a raised central column in the apparatus and the further presence of a hydraulically operated vacuum-tight lid permits but little air to enter the composition during processing. Thus, the gelling agent and a portion of liquid including water and/or humectant can be efficiently blended in the "Unimix" apparatus. Then the remaining liquid can be separately blended with the polishing agent and additional components (except for post-added components, such as flavouring oil) in the "Unimix" apparatus, and then the two dispersions blended together in the "Unimix" apparatus. If desired, the small amount of air can be largely removed under the depressurised conditions in the apparatus. The apparatus can be used to blend igredients at room temperature as well as at higher temperatures.

The following Examples illustrate the invention. All parts and proportions are by weight unless otherwise indicated and all sieve sizes are U.S. Standard.

Example 1

A transparent toothpaste having the following formulation is prepared: glycerine 25%, aqueous 70% solution of sorbitol 40%; cellulose gum (sodium carboxymethyl cellulose) 0.35%; colloidal silica (thickener, e.g. "Cab-O-Sil M5" manufactured by Cabot Corporation, U.S.A. or "Syloid 244", manufactured by Grace, Davison Chemical Co., U.S.A., having a bulk density of 0.11 g/cm^3) 3.5% "Syloid 74" 18%; detergent (sodium lauryl sulphate) 2%; added water about 6%; the balance being a trace of blue dye (e.g. 0.1% of F. D. and C, blue No. 1, added as a 1% aqueous solution), preservatives and flavours. This transparent toothpaste is mechanically blended with 2% of mother of pearl flakes (of a size, previously described, retained on a 100 mesh sieve and passing through a 40 mesh sieve). When the resulting transparent sparkling dentifrice is tested for its ability to remove stains from human dental enamel it is found to be about 34% more effective than a similar dentifrice free of the mother of pearl flakes.

In the stain removal test, sections of human dental enamel are etched with 0.1N HCl for 2 minutes, rinsed with water, then wetted with a dilute solution of stannous fluoride, wiped dry, and finally exposed to a stream of hydrogen sulphide gas which results in the deposition of a brown deposit of stannous sulphide. The amount of stain on the surface is measured with a "Gardner Automatic Colour Difference Metre". The surface is then brushed with a mechanical brushing machine for 3000 reciprocal strokes with a slurry of the dentifrice and the residual stain measured with the metre. Finally, the stain which remains is completely removed with dental pumice and the reflectance of this surface is read. The ability of a dentifrice to remove the stain is expressed by Equation 1.

$$\text{Equation 1) Percent Stain Removed} = \frac{(R_d \text{ 3000 strokes} - R_i \text{ initial}) \, 100}{R_d \text{ pumiced} - R_d \text{ initial}}$$

where R_d initial, R_d 3000 strokes, and R_d pumiced are respectively the reflectance values measured on the initially stained surface, after brushing for 300 reciprocal strokes and after removing the residual stain by pumicing.

Example 2

Example 1 is repeated using 25% of the TiO_2 coated mica flakes previously described in place of the mother of pearl flakes. An opaque cream having a pearlescent character is obtained, which has stain removal properties similar to those of Example 1.

Example 3

Example 1 is repeated, using 0.25% of "Rona MP10" flakes (TiO_2-coated mica flakes, the longest demensions of most flakes being 50 to 80 microns.

In the preferred embodiment of the invention a clear transparent toothpaste is used as other matrix in which the flakes are dispersed. Typically, the transparency of the matrix is such that one can easily read ordinary print (e.g. newspaper print) through an 8mm thick extrudate of the transparent toothpaste. It is within the scope of the invention, however, to add the flakes to a matrix which is somewhat hazy, or less desirably, merely translucent or even opaque, and to use larger proportions of the flakes (e.g. 10% or 15% or more) to give an iridescent or sparkling effect. Opaque matrices may contain polishing agents whose index of refraction is considerably different from that of the vehicle, e.g. $Al_2O_3.3H_2O$, $Ca_2HPO_4.2H_2O$ and chalk.

It is also within the scope of the invention to incorporate the pearlescent flakes into dentifrices other than toothpastes, e.g. toothpowders and crushable tooth tablets.

As is well known, mother of pearl (nacre) consists of prismatic psuedo hexagonal aragonite ($CaCO_3$ of refractive index 1.6809) crystals oriented so that the long crystallographic axis is at right angles to the plane of the platelets which are held together by conchiolin, a hornlike organic secretion.

The preferred pearlescent materials have parallel layers which are less than 1 micron in thickness and which produce interference colours by refraction of light. The indices of refraction of these materials are generally different from the index of refraction of the transparent toothpaste; for instance in one preferred embodiment the latter is in the range 1.4 to 1.5.

Example 4

The following transparent toothpaste is blended with 2% of mother of pearl flakes of a size such that 100% are retained in a 100 mesh sieve while passing through a 40 mesh sieve:

Toothpaste

Components	Parts
Glycerine	15
Sorbitol (70%)	45
Sodium carboxymethyl cellulose	0.7
"Syloid 244"	5
Sodium aluminosilicate	16
Sodium lauryl sulphate	2
Sodium benzoate	0.5
Sodium saccharin	0.2
Colour	0.2
Flavour	1
Chloroform	2.5
Water	3

WHAT WE CLAIM IS:—

1. A dentifrice containing non-toxic iridescent or pearlescent flakes.

2. A dentifrice as claimed in Claim 1 in which the flakes are dispersed in a toothpaste.

3. A dentifrice as claimed in Claim 2 containing 0.1% to 5% by weight of the flakes dispersed in a transparent toothpaste.

4. A dentifrice as claimed in any one of the preceding claims containing non-toxic iridescent or pearlescent flakes of less than 590 micron particle size.

5. A dentrifice as claimed in Claim 3 containing mother of pearl flakes of less than 590 micron particle size.

6. A dentifrice as claimed in Claim 5 in which the concentration of the mother of pearl flakes is in the range 1.5% to 3% by weight, the dentifrice when extruded as a ribbon 4mm to 8mm thick being clear with visible spaced light refracting dots.

7. A dentifrice as claimed in Claims 3 and 4 containing iridescent mica flakes, coated with another material whose refractive index is different from that of mica.

8. A dentifrice as claimed in Claim 7 in which the mica flakes carry layers of titanium dioxide.

9. A dentifrice as claimed in Claim 8 containing mica flakes having layers of titanium dioxide thereon and having length dimensions of less than 100 microns, in a concentration of 0.1% to 0.3% by weight,

the dentifrice when extruded as a ribbon 4mm to 8mm thick having an opaque pearlescent appearance.

10. A dentrifice as claimed in Claim 1 and substantially as described in any of the Examples.

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